

Summary of Simplified Two Time Step Method for Calculating Combustion Rates and Nitrogen Oxide Emissions for Hydrogen/Air and Hydrogen/Oxygen

Melissa Molnar
Ohio University
Athens, Ohio 45701

C. John Marek
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Abstract

A simplified single rate expression for hydrogen combustion and nitrogen oxide production was developed. Detailed kinetics are predicted for the chemical kinetic times using the complete chemical mechanism over the entire operating space. These times are then correlated to the reactor conditions using an exponential fit. Simple first order reaction expressions are then used to find the conversion in the reactor. The method uses a two time step kinetic scheme. The first time averaged step is used at the initial times with smaller water concentrations. This gives the average chemical kinetic time as a function of initial overall fuel air ratio, temperature, and pressure. The second instantaneous step is used at higher water concentrations ($>1 \times 10^{-20}$ moles/cc) in the mixture which gives the chemical kinetic time as a function of the instantaneous fuel and water mole concentrations, pressure and temperature (T_4). The simple correlations are then compared to the turbulent mixing times to determine the limiting properties of the reaction.

The NASA Glenn GLSENS kinetics code calculates the reaction rates and rate constants for each species in a kinetic scheme for finite kinetic rates. These reaction rates are used to calculate the necessary chemical kinetic times. This time is regressed over the complete initial conditions using the Excel regression routine. Chemical kinetic time equations for H_2 and NO_x are obtained for H_2 /Air fuel and for H_2 /O₂.

A similar correlation is also developed using data from NASA's Chemical Equilibrium Applications (CEA) code to determine the equilibrium temperature (T_4) as a function of overall fuel/air ratio, pressure and initial temperature (T_3). High values of the regression coefficient R^2 are obtained.

Introduction

Hydrogen is the fuel of the future. Iceland is converting their economy to hydrogen and several countries (United States, Germany, Australia, Mexico, China, Canada, Japan, and Russia) are strongly interested in the technology because of global warming concerns from CO₂ and the unlimited supply of hydrogen from water conversion. It is important to have a simple, quick method of computing the chemical rates for prediction of times of conversion and for the design of combustors. Accurate chemical kinetic mechanisms exist for hydrogen reaction, but they involve as many as 21 chemical steps with the production of intermediate species like OH, HO₂, H and O atoms with H₂O₂ as an intermediary. We have used the H₂ mechanism of S.L. Hwang, et al. (ref. 1) as the basis of this report. No changes in the hydrogen mechanism were made in switching from H₂/Air to H₂/O₂. We have taken a forty-two step mechanism for the production of nitrogen oxides from GRI-Mech 2.1 without the carbon reactions, used in reference 2, and correlated the formation rate of nitrogen oxides in the presence of hydrogen by a similar two time step method. Any detailed mechanism could have been used to compute the chemical kinetic time constants.

The hydrogen reactions are about seven times as fast as hydrocarbon fuels and the reactions require small time steps to integrate accurately. We have used the NASA Glenn GLSENS kinetics code (ref. 3), to integrate the progress of the reaction accurately. The classical methods were used to compute over two thousand cases at constant T and P. Then the results were correlated with a simple two time step approach to predict the chemical kinetic time constants. The derived method involves only the principal species H₂, and H₂O and NO_x for nitrogen oxides, species which are predicted routinely by computer codes. We do not require tracking the intermediate free radicals, as the kinetic times in step one before the radicals become large are practically constant and in step two are related to the instantaneous H₂, O₂, and H₂O concentrations.

This report is a summary of a more detailed summary report (ref. 4). The two time step approach was used successfully by Molnar and Marek in reference 2 for Jet-A and methane. The two time step approach is used because the free radicals OH, etc., catalyze the reactions and act as important intermediates. The principle reaction for water production is OH through the reaction:



We think that the more water that is present in the reactor then the more OH would be present accelerating all of the reactions. So H₂O can be used as an indicator of the OH present.

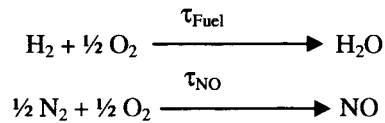
In order to obtain the chemical source term, a comparison can be made of the turbulent mixing time τ_m or k/ϵ with k being the turbulent kinetic energy, ϵ is the dissipation rate and the chemical kinetic time τ_c , and the longest time is used as the overall time (ref. 5). This may also be represented by the following relationship:

$$\tau = \max (\tau_m, \tau_c)$$

With the approach derived here, a simple direct comparison can be made between the mixing and chemical kinetic times and the minimum rate used for all points and at each iteration of a CFD code.

Simple Model Equations

Only the following equations can be used to model the chemical system.



The following first order reaction is used to represent the rate of fuel burning. We compute the net reaction time so we do not worry about the forward and reverse processes, only the net process. We assume that the fuel goes to zero at the end of the reaction and that the NO_x increases linearly and it is far from equilibrium. (In this report, t and τ are given in milliseconds, while concentrations are given in gmol/cc):

$$\frac{d\text{H}_2}{dt} = -\frac{c\text{H}_2}{\tau_{\text{H}_2}}; \text{ SO } \tau_{\text{H}_2} = -\frac{c\text{H}_2}{\sum \left(\frac{d\text{H}_2}{dt} \right)}; \text{ OR if } \tau_{\text{H}_2} \text{ is constant: } \text{H}_2 = \text{H}_{2_0} e^{\left(\frac{-t}{\tau_{\text{H}_2}} \right)}$$

The chemical time τ_{H_2} can be computed from the concentration of H_2 and its net rate of production.

The nitrogen oxide formation rate, a species important for combustor emissions, was modeled as a simple zero order expression.

$$\text{NO}_x = \frac{t}{\tau_{\text{NO}_x}^*}; \text{ OR } \tau_{\text{NO}_x} \text{ is constant } \frac{d\text{NO}_x}{dt} = \frac{1}{\tau_{\text{NO}_x}^*}$$

where $\tau_{\text{NO}_x}^*$ has units of $\frac{\text{ms} \cdot \text{cc}}{\text{gmol}}$

H₂/Air Initial conditions for chemical kinetic

Temperature = 1000, 1500, 2000, 2500 K
Pressure = 1, 10, 20, 30, 40 atm
Lean equivalence ratios = 0.3 to 1.0 increments of 0.1
Rich equivalence ratios = 1.05, 1.1 to 2.0 increments of 0.1

H₂/O₂ Initial conditions for chemical kinetic times for advanced rocket combustors (ref. 6)

Temperature = 1000, to 4000, increments of 500, then 5000 K
Pressure = 0.5, 1.0, 10, 50, 100, 200, 300, 400 atm
Lean equivalence ratio = 0.1 to 1.0 increments of 0.1
Rich equivalence ratio = 1.05, 1.1, 1.2 to 3.0 increments of 0.2
Time steps for Step 2 were the same as Step 1 with integration to 3 milliseconds. The output tabulated at least 20 points per case. For the approximately 2000 cases, the total number of points correlated could exceed 40000 per regression. Excel can handle up to 65000 points.

The kinetic mechanism of Hwang, S.M., et al. (ref. 1), next page, was used for the full range of conditions without modification.

Even though the mechanism was tested to a temperature of 3000 K and 4 atmospheres, we felt that the mechanism would extrapolate and give reasonable results for design because nothing else was available at the high temperature and high pressure conditions. The differences between the H₂/Air and the H₂/O₂ is the absence of nitrogen in the H₂/O₂ set, and in H₂/O₂ the maximum temperatures were twice that of H₂/Air and the maximum pressures were an order of magnitude higher. We computed and correlated the chemical kinetic times over the full range of conditions.

H₂ Kinetic Scheme for Step 1(Average) and Step 2 (Instantaneous) Methods

CC S.M. Hwang, et al. (ref. 1) H₂ Combustion Over a Range of Conditions

| | | | | | | |
|---|-------|-----|-----------|-----|------------|----------------|
| &RTYPE GLOBAL=TRUE,GRONLY=FALSE. &END | | | | | | |
| H | O2 | = | OH | O | 6.73 E+15 | -0.499 16671.6 |
| O | H2 | = | OH | H | 5.06 E+04 | 2.67 6289.2 |
| OH | H2 | = | H2O | H | 2.16 E+08 | 1.510 3430.0 |
| O | H2O | = | 2.OOH | | 4.51 E+04 | 2.7 14551.4 |
| O | O | = | O2 | M | 1.00 E+17 | -1. 0.0 |
| THIRDBODY | | | | | | |
| H2O | 18.5 | H2 | 2.9 | O2 | 1.2 | END |
| H | H | = | H2 | M | 6.4 E+17 | -1. 0.0 |
| THIRDBODY | | | | | | |
| H2O | 12.0 | H2 | 4.0 | H | 26. | END |
| H | O | = | OH | M | 6.2 E+16 | -0.6 0.0 |
| THIRDBODY | | | | | | |
| H2O | 5. | | | | | END |
| H | OH | = | H2O | M | 8.4 E+21 | -2. 0.0 |
| THIRDBODY | | | | | | |
| H2O | 16.25 | H2 | 2.5 | | | END |
| H | O2 | = | HO2 | M | 5.55 E+18 | -1.15 0.0 |
| THIRDBODY | | | | | | |
| H2O | 21.3 | H2 | 3.33 | O2 | 1.33 | END |
| HO2 | H | = | OH | OH | 8.4 E+13 | 0.0 635.0 |
| HO2 | H | = | H2 | O2 | 2.5 E+13 | 0.0 693.1 |
| HO2 | H | = | H2O | O | 5.0 E+12 | 0.0 1410.1 |
| HO2 | O | = | O2 | OH | 2.0 E+13 | 0. 0. |
| HO2 | OH | = | H2O | O2 | 2.0 E+13 | 0. 0. |
| HO2 | HO2 | = | H2O2 | O2 | 1.3 E+11 | 0. -1630.0 |
| HO2 | HO2 | = | H2O2 | O2 | 4.2 E+14 | 0. 1999.5 |
| M | H2O2 | = | 2.OOH | M | 1.2 E+17 | 0. 45506.7 |
| THIRDBODY | | | | | | |
| H2O | 6.0 | O2 | 0.78 | | | END |
| H2O2 | H | = | HO2 | H2 | 1.7 E+12 | 0. 3776.3 |
| H2O2 | H | = | H2O | OH | 1.0 E+13 | 0. 3585.1 |
| H2O2 | O | = | HO2 | OH | 2.8 E+13 | 0. 6405.4 |
| H2O2 | OH | = | H2O | HO2 | 1.0 E+12 | 0. 0. |
| H2O2 | OH | = | H2O | HO2 | 5.75 E+12 | 0. 9559.8 |
| N | NO | = | N2 | O | 3.500E+13 | .000 330.00 |
| N | O2 | = | NO | O | 2.650E+12 | .000 6400.00 |
| N | OH | = | NO | H | 7.333E+13 | .000 1120.00 |
| HO2 | NO | = | NO2 | OH | 2.110E+12 | .000 -480.00 |
| NO | O | = | NO2 | M | 1.060E+20 | -1.410 .00 |
| THIRDBODY | | | | | | |
| H2 | 2.00 | H2O | 6.00 | N2 | 0.625 | END |
| NO2 | O | = | NO | O2 | 3.900E+12 | .000 -240.00 |
| NO2 | H | = | NO | OH | 1.320E+14 | .000 360.00 |
| PLUS 33 REACTIONS FOR N2O, NH, NH2, NNH, HNO, and NH3 | | | | | | |
| H | O2 | | H2O | = | HO2 | H2O |
| 1. | 1. | 1. | 9.380E+18 | | -.760 .00 | |
| H | O2 | | N2 | = | HO2 | N2 |
| 1. | 1. | 1. | 3.750E+20 | | -1.720 .00 | |

Some reactions are bimolecular and some are trimolecular expressions so the kinetics code GLSENS was used.

Correlation Results

Equilibrium Lean and Rich H₂/Air Correlations

The H₂ equilibrium correlation for T_4 was correlated for both the lean and rich cases (ref. 7). The exponential function did not correlate the complete data over the total equivalence ratio from 0.2 to 2.0, because of the peak in the values at the stoichiometric conditions. We chose to correlate the values from lean ($\phi = 0.2$ to 1.) and then rich from ($\phi > 1.05$ to 2.0). A similar approach was used for the chemical kinetic times. The T_4 equations were correlated over the complete temperature, pressure and equivalence ratio Φ : The stoichiometric Φ was included on the lean side.

$$T_4 = A(P)^a (T_3)^b (\Phi)^c$$

Although these equations seem complex, they are simple to program and use. Calculations can even be done on a hand calculator.

| | A | a | b | c | R-squared |
|------------|--------|---------|-------|--------|-----------|
| Lean T_4 | 476.9 | 0.00419 | 0.261 | 0.432 | 0.936 |
| Rich T_4 | 1217.0 | 0.00727 | 0.120 | -0.243 | 0.962 |

R-square values have been included to demonstrate the strength of the correlation. R-squared is a measure of the error in the model; an R-squared value of one is ideal. The good R^2 values obtained are typical of all the variables.

Chemical Kinetic Times for H_2 /Air

Step One Equations for H_2 /Air Chemical Kinetic Time Correlations

The following form of equation was used for the H_2 and NO_x step one correlations:

$$\tau = A(P)^a (\Phi)^b \exp\left[\frac{E}{T}\right]$$

where τ is the chemical kinetic time in milliseconds, P is pressure in atm, f/a is the initial or overall mass fuel air ratio as in reference 2, and T is the temperature in Kelvin. The correlation is switched to Step Two when the water molar concentration is greater than 1×10^{-20} moles/cc. This value was chosen arbitrarily as a simple switch. Step two can not be used with small concentrations of water because if the value of the water concentration were zero, the entire correlation time would go to zero or predict an infinite rate.

Step One H_2 /Air

| | | A | a | E | b | R-squared |
|------------|------|---------|--------|--------|--------|-----------|
| H_2 /Air | Lean | 1.82E-7 | 0.673 | 20580. | -0.128 | 0.794 |
| H_2 /Air | Rich | 2.48E-7 | -0.455 | 20044. | 0.661 | 0.900 |
| NO_x | Lean | 8.547 | -1.45 | 30928. | 0.169 | 0.895 |
| NO_x | Rich | 2115.6 | -1.60 | 25986. | 1.377 | 0.922 |

Step Two Equations for H_2 /Air

The following form of equation was used for both the τ_{H_2} step two fuel and NO_x correlations except for different constants. This form of the equation produced the best fit:

$$\tau = A(P)^a (cH_2)^b (cH_2O)^c \exp\left[\frac{E}{T}\right]$$

where P is pressure in atm, cH_2 is the instantaneous molar concentration of H_2 and cH_2O is the instantaneous water concentration, moles/cc, and T is the mixture temperature in Kelvin. We have correlated to only the major species hoping that cH_2O will track the minor species (OH, H, O, etc.) to allow good overall correlation and easy to use equations.

Step Two H_2 /Air Chemical Kinetic Time Correlations

| | | A | a | E | b | c | R-squared |
|------------|------|----------|-------|--------|--------|--------|-----------|
| H_2 /Air | Lean | 3.06E-17 | 0.797 | 14991. | -0.855 | -0.870 | 0.825 |
| H_2 /Air | Rich | 1.99E-18 | 1.09 | 17980. | -0.923 | -0.769 | 0.914 |
| NO_x | Lean | 0.126 | -1.19 | 21201. | 0.348 | -1.02 | 0.943 |
| NO_x | Rich | 9.302E-4 | -2.15 | 22305. | 0.978 | -0.754 | 0.946 |

H_2/O_2 Equilibrium Correlations

The H_2/O_2 presentation closely follows the H_2 /Air presentation.

$$T_4 = A(P)^a (\Phi)^b (T_{3H_2})^c (T_{3O_2})^d$$

Equilibrium Lean and Rich H₂/O₂ Correlations

| | A | a | b | c | d | R-squared |
|---------------------|-----------|--------|--------|-------|-------|-----------|
| Lean T ₄ | 1.46E-109 | 0.0248 | 0.393 | 8.96 | 58.4 | 0.91 |
| Rich T ₄ | 0.96 | 0.021 | -0.427 | 0.395 | 1.752 | 0.92 |

Again a good correlation is obtained.

Chemical Kinetic Times for H₂/O₂

Step One Equations for H₂/O₂

The lean and rich step one H₂/O₂ chemical kinetic time correlations are of the following form:

$$\tau = A(P)^a (\Phi)^b \exp\left[\frac{D}{T}\right]$$

where P is pressure in atm, Φ is the initial or overall equivalence ratio and T is the temperature in Kelvin.

Step One H₂/O₂ Chemical Kinetic Time Correlations

| | A | a | D | b | R-squared |
|------|----------|--------|--------|-------|-----------|
| Lean | 8.07E-07 | -0.648 | 19469. | 0.491 | 0.928 |
| Rich | 1.50E-06 | -0.713 | 18718. | 0.918 | 0.946 |

Step Two Equations for H₂/O₂

The following form of equation was used for all lean and rich H₂/O₂ step two correlations:

$$\tau = A(P)^a (c_{\text{Fuel}})^b (c_{H_2O})^c \exp\left[\frac{E}{T}\right]$$

Step Two H₂/O₂ Chemical Kinetic Time Correlations

| | A | a | E | b | c | R-squared |
|------|-----------|--------|--------|--------|--------|-----------|
| Lean | 9.832E-09 | -0.471 | 16964. | 0.325 | -0.596 | 0.930 |
| Rich | 1.621E-17 | 1.069 | 19794. | -1.255 | -0.590 | 0.941 |

Comparison of the Model With the Full Mechanism Kinetics

The predictions of the full mechanism (H₂, H, O, OH and H₂O) are plotted in figure1, and then our model predictions are superimposed on the calculations. The model predictions are close to the full mechanism predictions. The model used a very simple mass balance for the water concentration. We have not included the intermediate species in our predictions, but we correlate the chemical kinetic times to the overall species concentrations. The H₂O model concentration is higher than the full mechanism, because no intermediate H species exist in the model. The ignition delay time (3.E-4 milliseconds) is closely predicted. As expected, OH, H and O increase at almost the same rate as H₂O, so H₂O is a good indicator of the reaction rate.

Since we use the model predictions of concentration to predict the chemical kinetic times, we have correlated the full mechanism chemical kinetic times against the model concentrations of H₂ and H₂O. The chemical kinetic time for this condition is about one microsecond so the integration requires only about 3000 steps.

Reduced Model used

These simple equations in an Excel spreadsheet.

$$\text{INEFF} = \frac{c_{H_{2n}}}{c_{H_{2n-1}}} = \exp\left(-\frac{t_n - t_{n-1}}{\tau_F}\right)$$

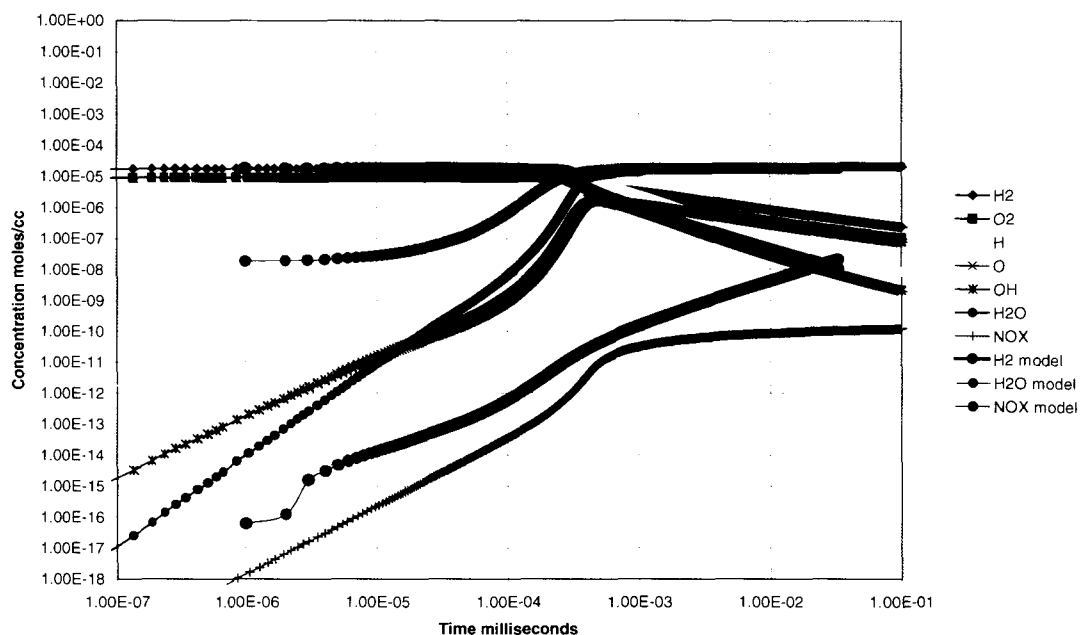
$$c_{H_{2n}} = c_{H_{2n-1}} * \text{INEFF}$$

$$c_{H_2O} = (c_{H_2}^0 - c_{H_2})$$

$$c_{NO_{xn}} = c_{NO_{xn-1}} + \frac{t_n - t_{n-1}}{\tau_{NO_x}}$$

Used backward differencing $\Delta t = 1.e-6$ for this comparison.

Figure 1. H₂/Air Concentration (Full Mechanism)
Compared to Reduced Model vs Time ms



Conclusions

A simplified kinetic scheme for H₂/Air and H₂/O₂ fuels resulted in a two time step correlation that calculates chemical kinetic times for fuel and NO_x. These models are simple enough to use in spreadsheet calculations and they are very accurate. These chemical kinetic time equations can then be used in a numerical combustor code to compare the chemical kinetic time with the turbulent mixing time at every grid point and for every iteration step. Strong step one and step two H₂ correlations were developed ($R^2 > 0.9$) for all relations, both the H₂/Air and H₂/O₂ correlations. However, because we are trying to correlate so many values over a wide range of conditions, error exists. These model equations are believed to be extremely useful in the comparison of kinetic reaction and turbulent mixing times and in the computation of kinetic rate results. In our model we have only two equations and four major species, therefore the step size can be large and the rates are no longer coupled.

References

1. S.M. Hwang; Si-Ok Ryu; K.J. De Witt; and M.J. Rabinowitz: Rate Coefficient Measurements of H + O₂ = Products Manuscript in Publication, August 2004
2. Molnar, Melissa; and Marek, C. John: New Reduced Two-Time Step Method for Calculating Combustion and Emission Rates of Jet-A and Methane Fuel. NASA/TM—2004-213046, April 2004.
3. Bittker, D.A.: GLSENS. A Generalized Extension of LSENS Including Global Reactions and Added Sensitivity Analysis for the Perfectly Stirred Reactor, NASA Reference Publication 1362, 1999.
4. Molnar, Melissa; and Marek, C. John: Simplified Two Time Step Method for Calculating Combustion Rates and Nitrogen Oxide Emissions for Hydrogen/Air and Hydrogen/Oxygen. NASA/TM—2005-XXXXX, DDDD 2005.
5. Brink, Anders; Mueller, Christian; Kilpinen, Pia; and Hupa, Mikko: Possibilities and Limitations of the Eddy Break-Up Model, Combustion and Flame, 123, 275–279 (2000).
6. Breisacher, Kevin, J.; Personal Communication NASA Glenn Research Center, Combustion Branch, March 2004.
7. Sanford, Gordon; and McBride, Bonnie J.: Computer Program for Calculation of Complex Chemical Equilibrium Composition and Applications. NASA Reference Publication 1311, October 1994.